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(Project No ADC-516)

AN EVALUATION OF A COMMERCIAL INSTRUMENT FOR CHLORDANE AND HEPTACHLOR SAMPLING

By

Thomas C. Thomas, Chemist
Jerry W. Jackson, Capt, USAF, BSC

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U S A F ENVIRONMENTAL HEALTH LABORATORY
McCLELLAN AFB, CA. 95652

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Several problems are associated with operation of the sampler. Suggested improvements are discussed in the report. Suggestions for further work are also included.

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Prepared By:

THOMAS C. THOMAS
Chief, Air & Inst. Analysis Branch

JERRY W. JACKSON
Capt, USAF, BSC
Chief, Special Projects Branch

Reviewed By:

JOHN J. GOKELMAN
Major, USAF, BSC
Chief, Environmental Protection Engrg Div.

Approved By:

DONALD D. HIGGINS
Lt Col, USAF, BSC
Commander

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ABSTRACT

A commercial pesticide sampler was evaluated for chlordane and heptachlor sampling. The sampler can obtain samples at rates up to 6.5 CFM through each of two collectors. Collectors are glass fiber filters impregnated with a polymeric medium. Chlordane and heptachlor appear to be collected by several modes: filtration, adsorption, diffusion and gas-solid partitioning.

Analyses showed that the compounds were collected efficiently on the collector and retained. A detection level of approximately 20 parts per trillion can be obtained with a one hour sample. The sampler is flexible and quite easy to use.

Several problems are associated with operation of the sampler. Suggested improvements are discussed in the report. Suggestions for further work are also included.

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1. Introduction:

a. Background:

At the request of Dr Henry F. Enos (Letter, Appendix I, Environmental Protection Agency, Washington DC), the USAF Environmental Health Laboratory (USAFEHL-M) agreed to evaluate a new commercial instrument designed to sample pesticides from air. Dr Enos wanted a quick and brief evaluation of this sampler and felt it could best be accomplished by the USAFEHL-M. He was aware of similar studies accomplished earlier by members of the laboratory (Ref. 1 & 2) working with various pesticides.

Dr Enos was particularly interested in having the sampler evaluated for collection efficiency of chlordane and heptachlor. These two pesticides have been the topic of much discussion because of their longevity, similar to such "hard" pesticides as DDT. Like DDT, chlordane and heptachlor have been widely used around homes and gardens. There is now evidence that these two pesticides may be more harmful than originally thought (Ref. 3 & 4). This laboratory is also involved in evaluating the airborne concentrations of chlordane in base housing at an Air Force base.

b. Objectives:

There were two objectives of this study. The first was to evaluate the trapping medium (collector) for pesticide collection efficiency and retention.

The second was a critical engineering evaluation of the sampler system, including engineering design, simplicity of use, and capability to sample constant and known volumes of air.

2. Experimental:

a. General:

Analytical pesticide standards were obtained from the Environmental Protection Agency, Research Triangle Park, North Carolina. "Nanograde" or equivalent solvents were used throughout the study. The samplers and collectors were manufactured by the Environmental Research Corporation (Figure 1 & 2). The samplers are capable of operating in either a 24V-DC or 120V-AC mode. Only the 120V-AC mode was used during the study. Both collector sites were used on the sampler

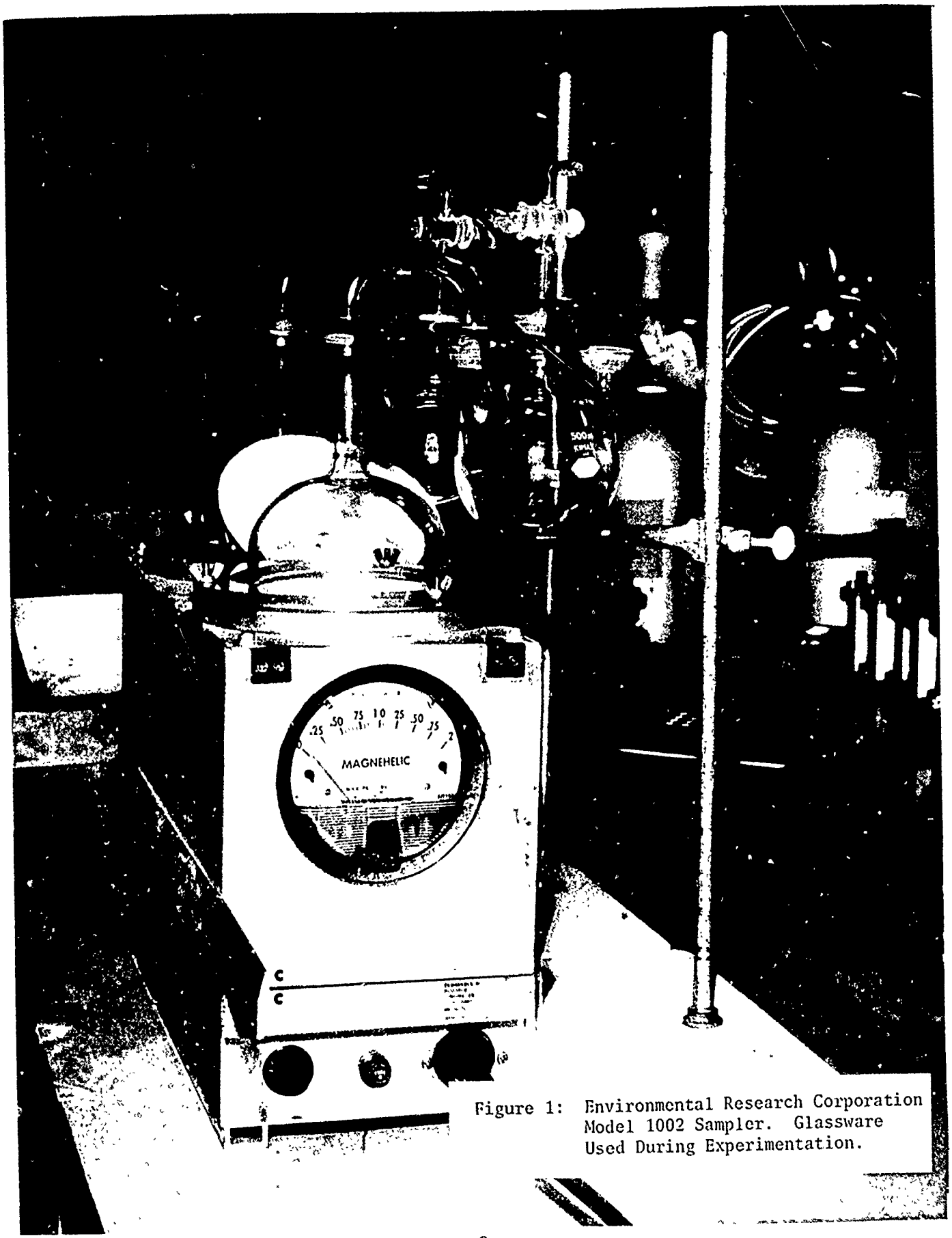

Figure 1: Environmental Research Corporation Model 1002 Sampler. Glassware Used During Experimentation.

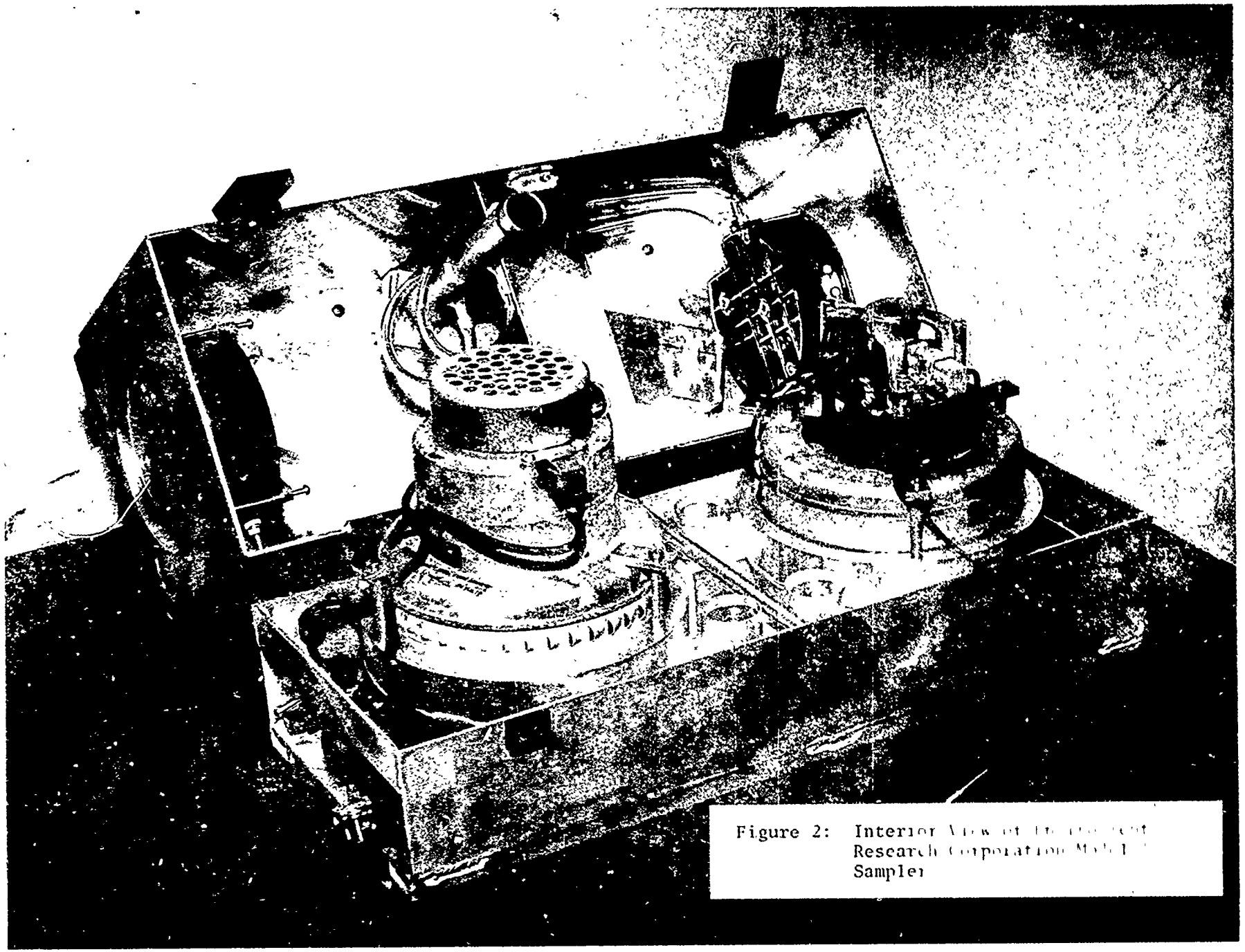

Figure 2: Interior View of the [illegible] Research Corporation Model [illegible] Sampler

in each experiment; one for chlordane and the other for heptachlor. The collector used to trap the pesticides was a filter pad 6" in diameter and 1/4" thick.

b. Gas Chromatograph:

A Varian Model 1200 gas chromatograph was used (Scandium electron-capture detector). It contained a 180 cm. x 3.2 m.m. o.d. glass column of 2.5% DC-200 and 0.5% carbowax 20 M on Gas Chrom Q, 60/80 mesh. Nitrogen carrier flow was 40 ml/min. Column, injector, and detector temperatures were respectively 170° C, 175° C, and 235° C. Retention times were tabulated and peak areas determined by using the gas chromatograph coupled to a Hewlett-Packard Model 3352B Laboratory Data System. Chlordane gave seven main peaks under the gas chromatographic conditions used. The data system was calibrated on each peak so that the total area was based on proportional amounts from each peak response.

c. Procedures:

Before use, all collectors were precleaned. Each collector was placed in a Buchner funnel, washed with 200 ml portions of acetone and hexane and dried by suction. This precleaning was necessary to obtain acceptable electron-capture detector background levels (Figure 3).

To determine pesticide retention, solutions of chlordane and heptachlor standards in hexane were placed on the collector with volumetric pipets. The solutions were deposited as uniformly as possible over the entire collector area and 5-10 minutes allowed for hexane evaporation. The samplers were then turned on and flows adjusted to 5-6 CFM. This technique was biased against the medium since under actual field conditions the sampler would collect the pesticides gradually, but it gave a good indication of retention.

To evaluate collection efficiency the glass apparatus shown in Figure 1 was used to generate pesticide vapors. Chlordane or heptachlor in the generator flask was vaporized at room temperature into the air stream and carried to the collectors. This procedure approximated field conditions where pesticide vapors could be present.

After the desired volume of air had passed through the system, the sampler was turned off. Where appropriate, the glass apparatus was disassembled and quantitatively rinsed to remove unvolatilized pesticides. The collectors were folded, placed in a large Soxhlet extraction apparatus

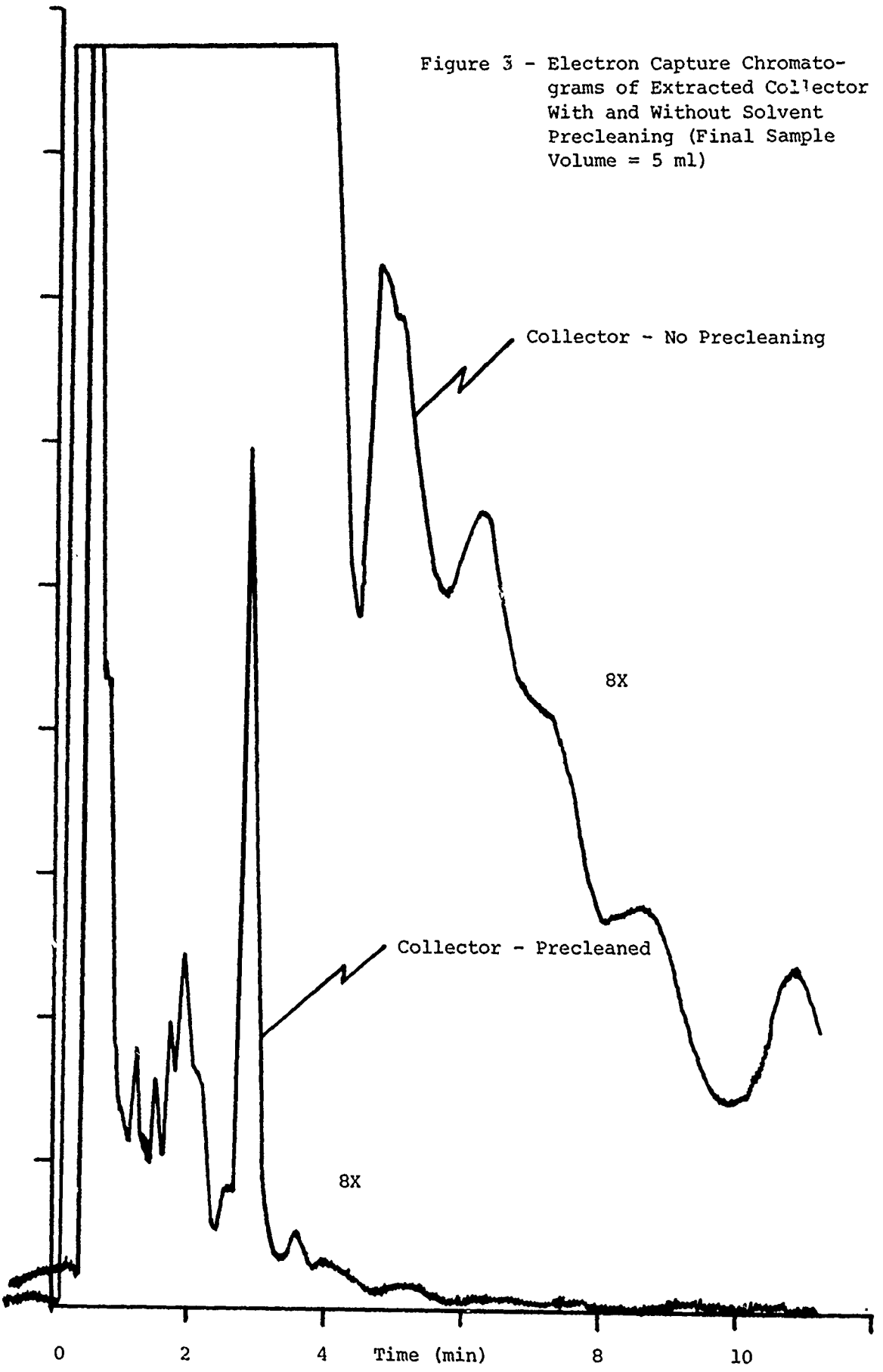

Figure 3 - Electron Capture Chromatograms of Extracted Collector With and Without Solvent Precleaning (Final Sample Volume = 5 ml)

and extracted with "Nanograde" hexane for three hours (15-20 exchanges per hour). Solvents were quantitatively concentrated in a rotary evaporator and diluted to final volume for gas chromatographic analysis.

3. Results of Retention and Efficiency Tests:

The concentration of pesticides used to evaluate the collector ranged from 0.8 to 14 $\mu g/M^3$. This laboratory is presently involved in a project to evaluate the airborne concentrations of chlordane in homes and the concentration levels being found are in this range. From Table I it can be seen that the collector proved to be quite efficient. In order to test collection efficiency and retention at maximum face velocity at the collector ("worst" case for collection efficiency) the sampling system was operated near maximum flow rates, 5-6 CFM (142-170LPM).

In experiments 4, 5, 9 and 10 the collectors were treated with known amounts of pesticide and various air volumes passed through them to evaluate the retention of the pesticides by the collector. Under field conditions it would not be expected that the pesticides would arrive all at once, but would be collected gradually over a period of time. However, this method of introduction was not considered a serious drawback, because if anything, the results were biased toward lower recoveries, owing to the relative volatility of the lower molecular weight compounds.

In experiments 6 and 7, pesticides were introduced to the collectors gradually in the form of vapors. This technique also possessed disadvantages, since the volatile fractions of chlordane, one of which is heptachlor, were more likely to be lost by revolatilization. Observation of the chromatograms in Figure 4 shows a larger proportion of the volatile fractions on the collector, whereas the solvent washings from the generator showed substantial amounts of the heavy fractions. However, this again biased the results toward lower recoveries.

4. Overall Evaluation:

a. Advantages Of This Sampler System:

The ability of this system to process large volumes of air and still have relatively good retention of chlordane and heptachlor, as shown in this study, is an advantage over most other systems. Collection of large samples not only reduces analytical difficulties such as detection limits, but provides enough trapped pesticides so that further confirmation, such as by mass spectrometry, can be performed.

TABLE I, COLLECTION EFFICIENCIES FOR CHLORDANE AND HEPTACHLOR BY THE ENVIRONMENTAL RESEARCH CORPORATION MODEL 1002 SAMPLER.

Experiment	Amount Introduced (µg)	Air Volume (M^3)*	Amount Unvaporized (µg)	Amount Found On Collector (µg)	Total Recovery (%)
#4[a]					
Chlordane	125	9.5	-	112	90
Heptachlor	33	11.2	-	31.1	94
#5[a]					
Chlordane	62.5	12.2	-	52.2	84
Heptachlor	22	10.3	-	23.5	107
#6[b]					
Chlordane	125	28.0	16.4	89.8	85
Heptachlor	110	27.2	1.4	73.9	68
#7[b]					
Chlordane	62.5	37.4	5.5	50.9	90
Heptachlor	55	30.6	<1	36.2	66
#9[a]					
Chlordane	125	22.4	-	86.7	69
Heptachlor	33	21.1	-	28.9	88
#10[a]					
Chlordane	125	43.0	-	89.5	72
Heptachlor	33	40.4	-	32.2	98

[a] Pesticides placed on collecting medium.

[b] Pesticides generated to collector as a vapor.

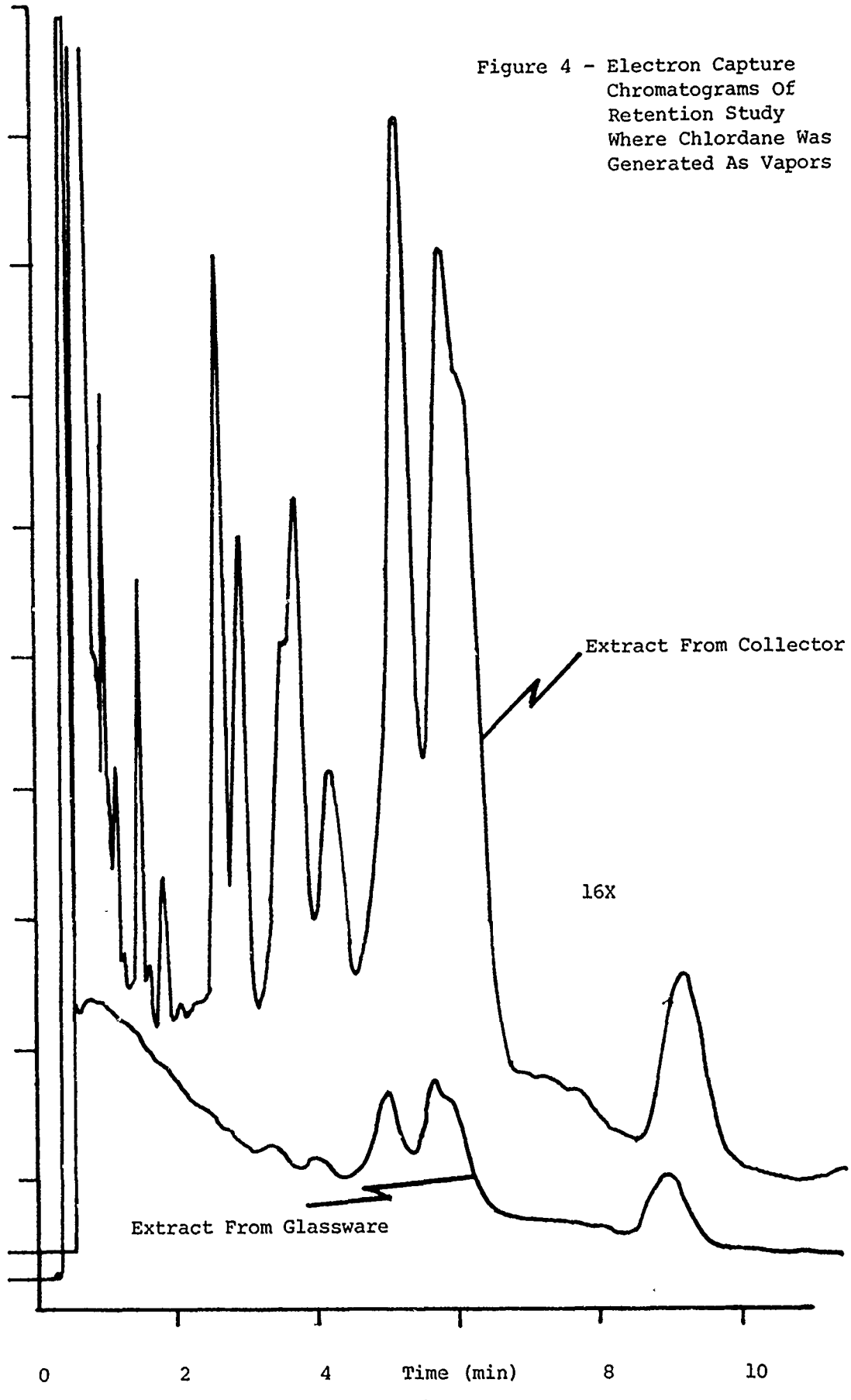

Figure 4 - Electron Capture Chromatograms Of Retention Study Where Chlordane Was Generated As Vapors

The collector uses several modes of collecting; filtration, adsorption, diffusion and gas-solid partitioning. In any case, the pesticides chlordane and heptachlor will be effectively collected whether they are in the vapor, aerosol or dust phase.

The sampling apparatus is much easier to operate in the field than solution-charged impingers and is simple enough so that technicians can be quickly trained in its operation. The operator has the option of setting the flow rate up to 6.5 CFM.

Quantitative removal and analysis of the pesticide from the collector is also simple. At the laboratory, the collectors are put through Soxhlet extraction, followed by concentration and cleanup. Precleaning of the collector for sampling is not involved.

The sample flow rate is measured by an orifice-Magnehelic® gauge arrangement. Generally, orifice flow measurement is accurate, trouble free and requires less frequent calibration than other methods.

The sampler operates from either of two power sources; 120V-AC or 24V-DC. The advantage of this flexibility is obvious. Ambient samples can be obtained in remote locations with power from a storage battery, a portable generator or automotive batteries.

b. Problems Encountered:

Several problems were noted in the use of this sampling system, the greatest being the collector is fragile. They are not rugged, and will crack or break into pieces if not handled carefully. When placing them on the sampler, extreme care must be taken when tightening down the wing nuts. If the collector cracks, channeling of flow may occur. Extreme care was taken with the collector in this study and even though no cracks were observed this could be the cause of the variability of results in Table I.

Another problem of this system is that it appears to be a non-specific collector. Experiments 1-3 were attempts to evaluate retention of the collectors by treating them with ~ 1.0 µg of the pesticides. After a one hour air sample was collected, the extracted sample showed a background that was intolerable, even after florisil column cleanup (Figure 5). Whether the sampler was positioned outside or in, it made no difference. Enough ambient dust was collected during a one hour period to form a visible deposit on the collector. With our analytical capability, an estimate

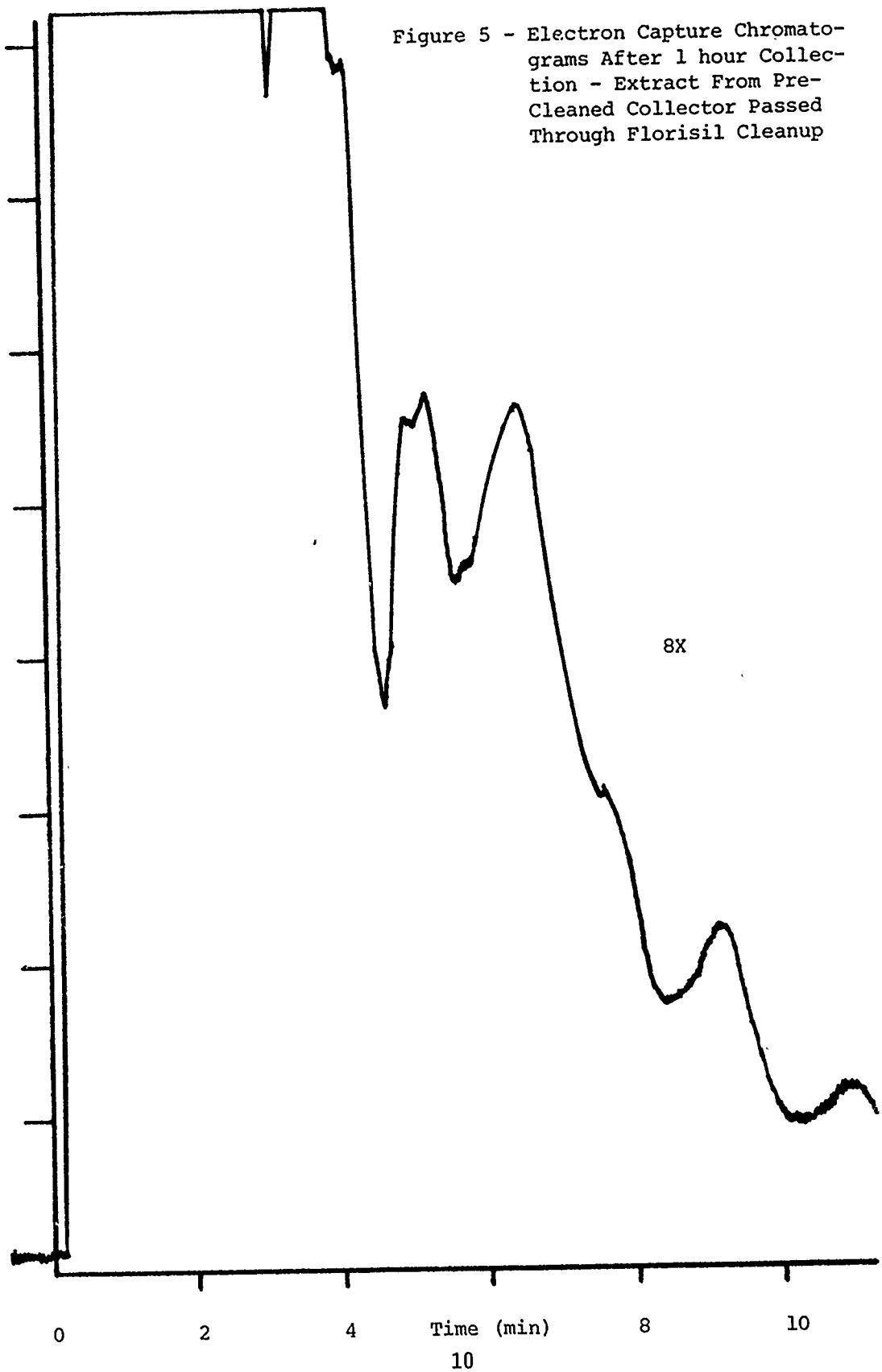

Figure 5 - Electron Capture Chromatograms After 1 hour Collection - Extract From Pre-Cleaned Collector Passed Through Florisil Cleanup

of our minimum detectability for chlordane caused by this background problem was 4 μg per filter (~20 PPT for a one hour sample). Use of a specific detector, the halogen microcoulometer, was investigated, but the background was still intolerable. Limited sensitivity of this detector required that the sample be concentrated even further. Other techniques of extraction and cleanup or use of different specific detectors may aid in resolving this difficulty.

A potential problem concerns possible recirculation of sampled air. The sampler expels gases horizontally from either end of the case. These gases are hot (~150°F) and tend to rise immediately. There is a good possibility that some gas will be recirculated when sampling in relatively calm air. Recirculation was observed in the laboratory using smoke tubes.

Another problem concerns temperature and the Magnehelic® gauge. The gauge has a maximum operating temperature of 140°F. The gas temperature inside the sampler case reaches 150° F within 10 minutes after sampling commences. Inaccuracies of measured volumes may be expected from this source.

c. Suggested Improvements In The Sampler System:

Two components of the sampler which should be improved in future models are the collector holding mechanism and the flow measurement mechanism.

As stated earlier, the collector is extremely fragile and cracks or breaks very easily. With the present mechanism, any amount of pressure can be applied to the collector and it is natural to tighten as much as possible for a good seal. Extreme care must be taken to avoid cracking the collector, and a good seal cannot be assured with the present mechanism. The present collector support is concave and has a slot around the perimeter. This combination places unnecessary stress on the collector. The support should be absolutely flat and rigid. The collector clamp should have a stop to avoid excessive pressure on the collector.

The flow measurement mechanism is basically a good one but can be improved. First, the Magnehelic® gauge on the tested model reads only 2" H_2O pressure maximum scale (6.5 CFM). This flow rate is reached at approximately one-half (50%) of motor power when operating on 120V-AC. The Magnehelic® gauge is easily damaged when exceeding

scale, which can occur easily with this system. The inadequate Magnehelic® unnecessarily restricts flow to approximately 50% of capacity. In view of the heating problem with the Magnehelic® gauges, they should be replaced with a dual, inclined liquid manometer of 5" H_2O pressure capacity. The manometer should be counter sunk in the side of the sampler.

5. Suggestions For Further Work:

The objectives of this work were to briefly evaluate the sampling system for collection efficiency of chlordane and heptachlor and to evaluate its engineering design. These objectives were accomplished, showing the system to be fairly efficient. It must be pointed out that this study was only a preliminary investigation and further work is necessary to reach conclusions concerning its efficiency for other pesticides.

Since this sampling system utilizes relatively high flow rates, chemical degradation of the pesticides once trapped could be a problem. This was not investigated in any detail during this study, however, this should be examined in depth because degradation reactions would be favored at high flow rates.

Another factor not studied was the influence of moisture on collection efficiency. Since this sampling system was designed for field use under all conditions, humidity could be an important factor.

Samples in this study were extracted using a Soxhlet apparatus. A simpler, faster method of extraction would be desirable. Simply placing the collector into a beaker with hexane and extracting in an ultrasonic unit for 30 minutes may give quantitative extractions (Ref. 5).

The 2" H_2O pressure Magnehelic® gauges should be replaced by expanded scale (5" H_2O) gauges and the sampler retested for collection efficiency and retention at greater sampling rates.

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APPENDIX I

LETTER, ENVIRONMENTAL PROTECTION AGENCY WASHINGTON DC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
RESEARCH AND DEVELOPMENT

Lt. Col. Phillip E. Smead
Headquarters, AFLC/SGB
Wright-Patterson Air Force Base
Ohio 45433

Dear Col. Smead:

This is in acknowledgment of our conversation on March 12 concerning the participation of Dr. T. Thomas, McClellan Air Force Base, in an evaluation study of a recently developed air sampler for chlordane and heptachlor. In discourse with Dr. H. Enos, Director of Equipment and Techniques Division, Dr. Thomas has expressed his interest in participating in this project which is expected to last 2-4 weeks.

It is understood that no overt expenses will be incurred by the Air Force (AF) as a result of Dr. Thomas' involvement in this study and that if required, the Environmental Protection Agency (EPA) will reimburse the AF for Dr. Thomas' time. If reimbursement is required, kindly inform me of costs and schedule and I will initiate an inter-agency agreement which will serve as the vehicle for transfer of funds. It is further understood that Dr. Thomas' participation will not take precedence over any AF programs with which he is associated.

Your cooperation in this joint AF/EPA endeavor is greatly appreciated.

Sincerely yours,

S. Sidney Verner

S. Sidney Verner

cc: Dr. T. Thomas
McClellan AFB